Discussion of “The Kinetics of the p-Toluquinhydrone Electrode” [F. Kornfeil (pp. 1674–1679, Vol. 119, No. 12)]

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vice versa may be neglected with respect to the rate at which the intermediate substance is produced and consumed in the two consecutive charge-transfer reaction steps. Under steady-state conditions, the continuity condition

$$i_1 \approx i_2 \qquad [1]$$

is established, where i_1 and i_2 are the C.D.'s carried by the two consecutive charge-transfer reactions. If there exists no other sources or sinks for the intermediate reaction products but consecutive charge-transfer reactions at the electrode interface, then this steady-state continuity condition is applicable to electrochemical reactions involving an arbitrary number of n consecutive charge-transfer steps, *i.e.*

$$i_\nu = i_{\nu+1} \qquad [2]$$

where $\nu = 1, 2, \ldots, n-1$. This case has been considered by Hurd.[30]

Referring to the work of Vetter,[28,29] Losev and Gorodetskii[20] have pointed out that the condition of small intermediate concentration is unnecessary. As I expressed in the paper under discussion my reservations concerning this point of view, I was indeed under the impression that Losev and Gorodetskii meant their comment to be true for the general case considered by Vetter. Losev's discussion of my paper and his recent publications[17,18,21,22] are most welcome. They give the special conditions, which Losev *et al.* assume to be adequate for using Eq. [2] above as a reliable basis for analyzing the current density overvoltage characteristics even at relatively high intermediate concentrations. These conditions are:

(*i*) The ratio of the electrode surface to the electrolyte volume is so large that during an electrolysis at constant potential rapid accumulation of the products of the electrochemical reaction in the bulk of the solution decreases any transient concentration gradients for the intermediate reaction products at the electrode surface within a reasonably short period of time to zero.

(*ii*) The intermediate concentrations in the bulk of the solution "remain always equal to zero," which may be the case when the intermediate products are unstable and enter into chemical reactions.

Knowing now the specific steady-state conditions considered by Losev, I still doubt that Eq. [2] above *i.e.*, the formalism derived elsewhere[20,28-30] provides a reliable basis for analyzing the current density overvoltage characteristics unless the intermediate concentrations are small compared to the concentrations of the most reduced substance (S_1) and most oxidized substances (S_{n+1}) entering into the consecutive charge-transfer mechanism

$$S_\nu \overset{i_\nu}{\rightleftharpoons} S_{\nu+1} + z_\nu e^-, \quad \nu = 1, 2, \ldots, n \qquad [3]$$

If condition (*i*) is satisfied, then the change in bulk concentration of all intermediate products must be generated in an anodic reaction from S_1 and in a cathodic reaction from S_{n+1}. Furthermore, not only the intermediate products are accumulated, but the concentration of S_1 decreases and the concentration of S_{n+1} increases in an anodic reaction (vice versa in the cathodic case) so that the equilibrium electrode potential rapidly approaches the externally imposed value, in which case the total C.D. approaches zero, *i.e.*, there is no true steady state under Losev's experimental condition.[28] A "quasi steady state" could be postulated if S_1 and S_{n+1} are available in much larger concentration than the intermediate products. In my opinion, the best and only way of characterizing the reliability of such an analysis of the current density overvoltage characteristics is to provide an error analysis for the deduced kinetic parameters.

Condition (*ii*) considered by Losev is not in conflict with what I have said in the paper under discussion, since I never objected to utilizing Vetter's analysis if the relative concentrations of the intermediate products are sufficiently small. I would like to point, however, to the fact that a finite equilibrium concentration of the intermediate products at the interface is required to establish an equilibrium potential characteristic of reaction [3] and to define the exchange C.D.'s of the various reaction steps. Since chemical reactions involving the intermediate products lead to branching in the equivalent mass flow at the interface, I do not believe that the interaction of consecutive charge-transfer reactions with chemical reactions is covered by the simple analysis given elsewhere.[20,28-30] In the general case, where the electrochemical reaction is controlled by charge-transfer, diffusion, and chemical reactions, the steady-state continuity condition Eq. [2] has to be replaced by

$$i_\nu = i_{\nu+1} + i^{D}_{\nu+1} + i^{R}_{\nu+1} \qquad \nu = 0, 1, 2, \ldots, n \qquad [4]$$

$$i_0 = i_{n+1} = 0$$

where $i^{D}_{\nu+1}$ and $i^{R}_{\nu+1}$ denote the equivalent C.D.'s with which the substance $S_{\nu+1}$ is consumed or produced at the interface via chemical reactions or by exchange with the bulk via diffusion. Note that no charge is carried across the interface by $i^{D}_{\nu+1}$ and $i^{R}_{\nu+1}$. I have treated in the paper under discussion the case of n consecutive charge-transfer reactions, when

$$i^{R}_{\nu+1} = 0$$

and

$$i^{D}_{\nu+1} = -\mathbf{F} D_{\nu+1} (\partial c_{\nu+1}/\partial x) \qquad [5]$$

If $i^{R}_{\nu+1} \neq 0$, then not only the diffusion of $S_{\nu+1}$ but also the diffusion of the reaction products has to be taken into account. The relation between the concentration of $S_{\nu+1}$ and the rate of the chemical reaction depends on the specific nature of the reaction. In general, the current densities carried by the various charge-transfer reaction steps will not be equal in this case, *i.e.*

$$i_\nu \neq i_{\nu+1} \qquad [6]$$

except for the very special condition

$$i^{D}_{\nu+1} = -\, i^{R}_{\nu+1}$$

I agree with Losev that, in the absence of chemical reactions, the interpretation of the steady-state c.d. overvoltage curve is considerably simplified if the diffusion currents of all intermediates are known from an independent set of experiments.

The Kinetics of the p-Toluquinhydrone Electrode

F. Kornfeil (pp. 1674-1679, Vol. 119, No. 12)

J. C. Reeve:[31] The following comments may be of interest not only to those considering Dr. Kornfeil's valuable results in the paper under discussion concerning consecutive charge-transfer reactions, but to those interested in such reactions in general.

The term "pseudo-Tafel region" was introduced by Hurd[30] to describe what seemed, from a point by point calculation, to be a linear region of the Tafel diagram between two limiting anodic situations (where the steps are separately "rate-determining," rather than simultaneously "rate-determining" as in the transition region). This was unfortunate, since there is in fact no such special region,[32] and any apparent pseudo-Tafel behavior in such cases simply arises from experimental or graphical lack of precision. Vetter, in his classic works cited by Dr. Kornfeil in the paper under discussion, made no claim for such a region. In the paper being discussed an additional complication is introduced in that its Eq. [8] is said to have "pseudo-Tafel form." In fact, this not only has normal Tafel form (as usual ignoring small possible changes in α_2 with

[30] R. M. Hurd, *This Journal*, 109, 327 (1962).

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[32] J. C. Reeve, *Coll. Czech. Chem. Comm.* (in English), 36, 757 (1971).

potential) but represents the normal anodic behavior complementary to the cathodic behavior indicated (the step $S_m \rightleftarrows S_o$ is "rate-determining" throughout). This behavior is marked as the "pseudo-Tafel region" in Fig. 4 of the paper under discussion but the short line shown at higher anodic overpotentials (where there has been a change of "rate-determining step") is very misleadingly called "the true Tafel line." Hurd[30] also called this region "the true Tafel-region," but only as opposed to the transition region, where there was supposed (incorrectly) to be an unexpected Tafelian behavior.

It is clear that terms such as "pseudo-Tafel behavior" and especially the term "pseudo-Tafel region" should be used with greater caution than hitherto.

Regarding the attainment of the steady state ($\gamma = 0.5$), it is said that (diffusion polarizations are to be supposed eliminated) "the stationary concentration of S_m can differ only slightly from its thermodynamic equilibrium concentration" for the given potential. In this statement it is not made clear between which solution species and S_m equilibrium is considered. In the here so-called pseudo-Tafel region, S_m will be in equilibrium with S_r. However, in the here so-called Tafel region, S_m can be in equilibrium with S_o at lower overpotentials and actually fall with increasing potential, but be nearly zero or again increasing at higher overpotentials (as in the present examples) depending on how closely α_1 approximates to α_2.[33]

It is possibly noteworthy that results, such as those used in Fig. 8 and 9 of the paper under discussion, can be used to determine i_o and both the sum and the difference of the reciprocal component current Tafel laws at $\eta \sim 0$ without making further suppositions.[34,35]

F. Kornfeil: I am grateful to the author of the above discussion for his interest and comments. I hope that the following arguments will help to remove at least the major part of any misunderstandings that may still exist.

First, and most importantly, it should be noted that, as a consequence of the experimental techniques used in the potential measurements, the transfer overpotential is the only component of the overpotential appearing in the experimentally determined values of the electrode potential. Since $\gamma \approx 0.5$, this means that all polarization curves presented are identical with the curves one would obtain from measurements in the steady state, if the diffusion coefficients of all reacting species and the rate constants of all chemical reactions involved in the reaction sequence were infinite. Therefore, the two charge-transfer steps clearly must proceed at equal rates over the entire range of overpotentials, irrespective of the sometimes very large difference between the individual exchange current densities $i_{0,1}$ and $i_{0,2}$.

Second, Dr. Reeve in the above discussion, is mistaken in his view that the phenomenon of the pseudo-Tafel lines is due to a lack of experimental or graphical precision. Inspection of Eq. [6] and [6a] of my paper under discussion reveals that, assuming $\gamma = 0.5$, at sufficiently large values of η, Eq. [6] simplifies to

$$i = 2i_{0,1} \exp\left(\frac{\alpha_1 \mathbf{F}}{RT}\eta\right)$$

with the intercept $2i_{0,1}$ in perfect analogy to the extrapolation of the Tafel line in a one-electron process. However, at intermediate values of η and the condition $i_{0,1} >> i_{0,2}$ the denominator of Eq. [6a] in the paper under discussion becomes unity and the numerator approximates $\exp(2\mathbf{F}\eta/RT)$ resulting, as pointed out by Vetter,[29] in another linear relationship between log i and η, namely

$$i = i_{0,2} \exp\left(\frac{1 + \alpha_2}{RT}\mathbf{F}\eta\right)$$

the pseudo-Tafel region, with the "wrong" intercept $2i_{0,2}$ (identical with the cathodic intercept), thereby raising the possibility of confusing an electrode reaction consisting of two consecutive charge-transfer steps with a single-step transfer of two electrons. What actually constitutes "sufficiently large" and "intermediate" values of the overpotential in this context depends on the kinetic parameters and their interrelations and has been clarified in Hurd's excellent analysis of this problem.[30]

If one remains faithful to the convention of referring to the linear portions as Tafel lines, then Hurd's terminology calling the straight line at the highest overpotentials the "true" Tafel line and the linear part of the polarization curve occurring at lower overpotentials the "pseudo"-Tafel line seems a most appropriate and logical choice. In view of the arguments presented above, it is, therefore, difficult to understand, both from the scientific and etymological points of view, why Dr. Reeve should find the term pseudo-Tafel region misleading. In fact, I fail to see any valid reason why electrochemists should, or the Ancient Greeks would, object to its continued use.

In regard to the last part of Dr. Reeve's discussion, the statement as to the small difference between the equilibrium and the steady-state concentrations of the intermediate should, in retrospect, have been presented in a more quantitative fashion. At any rate, a clear distinction should be made here between the steady-state concentration and the equilibrium concentration, a thermodynamic quantity governed by the equilibria existing among the quinone, meriquinone, semiquinone, and hydroquinone molecules. The assertion of the small concentration difference is based on considerations, via Faraday's laws, of the very small quantity of charge required for the observed rapid attainment of the steady-state condition.

[33] I. H. Plonski, *This Journal*, 116, 944 (1969).
[34] J. C. Reeve and G. Bech-Nielsen *Corr. Sci.*, 13, 351 (1973).
[35] K. B. Oldham and F. Mansfeld, *ibid.*, In press.

The Kinetics of Chlorine Evolution and Reduction on Titanium-Supported Metal Oxides Especially RuO_2 and IrO_2

A. T. Kuhn and C. J. Mortimer (pp. 231-236, Vol. 120, No. 2)

G. Faita and G. Fiori:[36] Kuhn and Mortimer ascribe, in the paper under discussion, the differences existing between their data and those of our work[37] mainly to experimental procedures.

The first objection concerns the method used for obtaining the necessary ohmic drop correction.

Kuhn and Mortimer in their paper describe the method used by us[37] as "short-circuiting the working electrode to the counterelectrode." This procedure would be obviously incorrect and as a matter of fact was not applied. The actual experimental arrangement is sketched in Fig. 1.

The transistor-driven mercury switch is placed across the cell terminals: but the cell is electrically isolated

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[37] G. Faita and G. Fiori, *J. Appl. Electrochem.*, 2, 31 (1972).

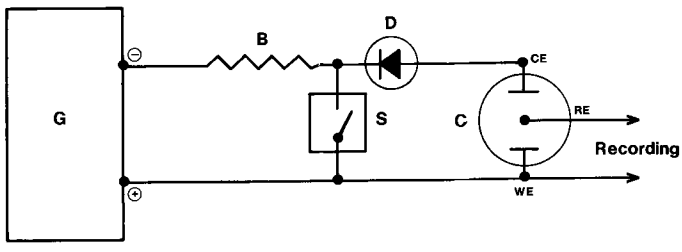

Fig. 1. Block diagram of the experimental apparatus used for ohmic drop correction. G, galvanostat; B, buffer resistor; D, diode; C, cell; S, mercury switch.